Nanomaterials for Water Purification

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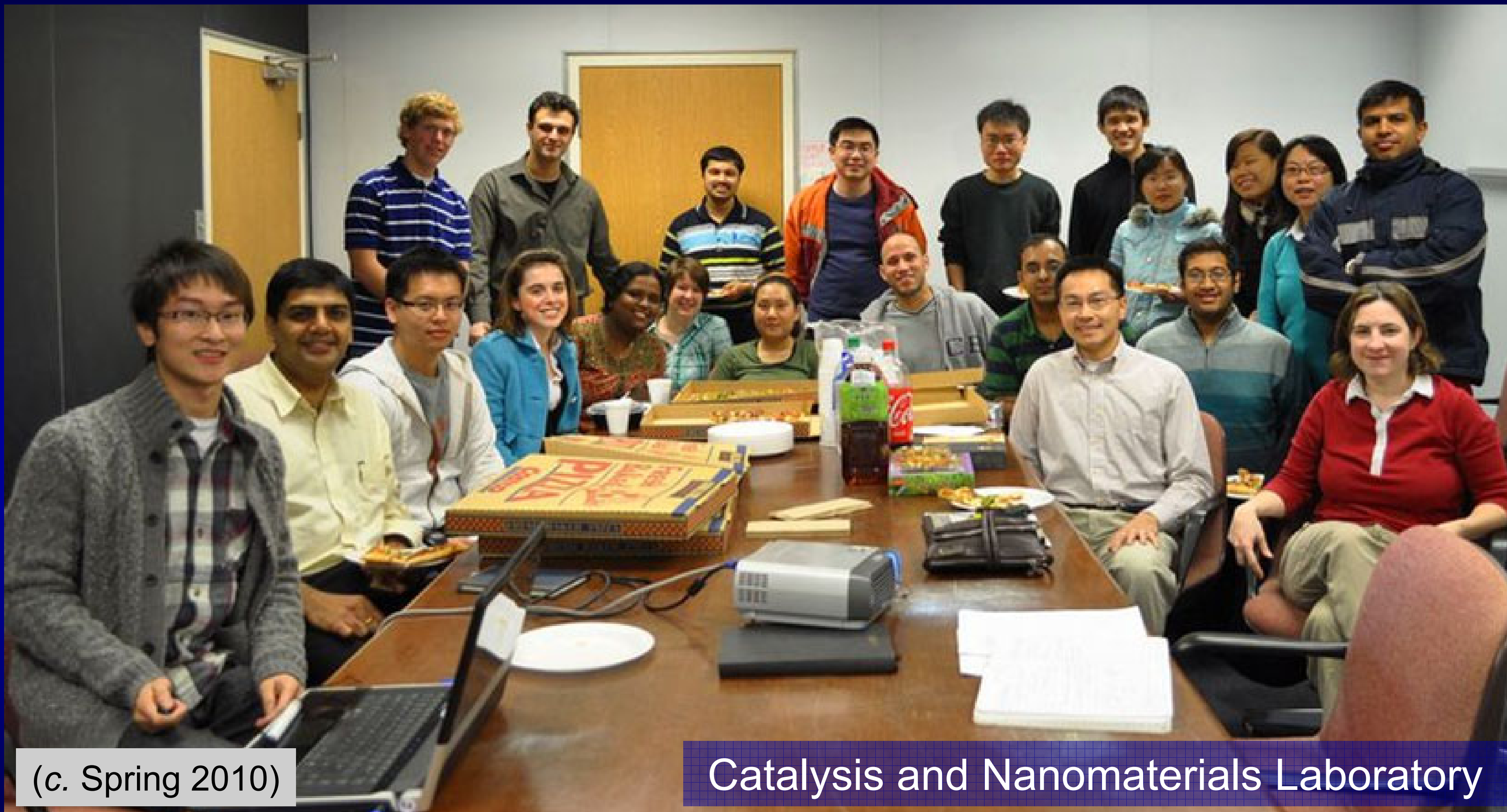
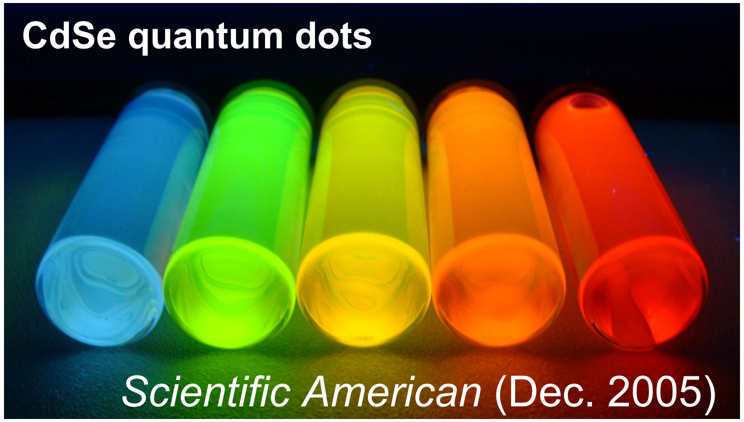
Acknowledgments



- National Science Foundation
- Smalley/Curl Award
- 3M
- Welch Foundation
- SABIC Americas
- WGC
- AEC

Areas of my research program



NP chemistry and scale-up

Pd-on-Au NPs

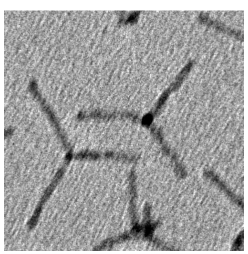
Water purification

$CHCl{=}CCl_2 + 4H_2$

$CH_3CH_3 + 3\ HCl$

NP catalysis

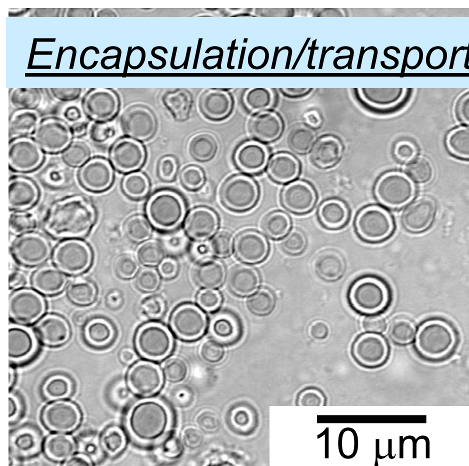
and tetrapods



50 nm

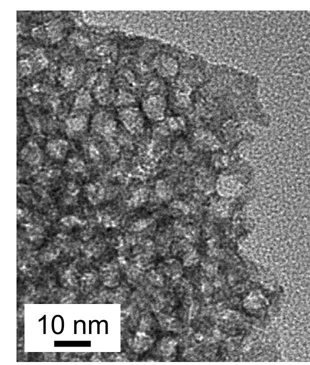
For use in solar cells

Encapsulation/transport/release

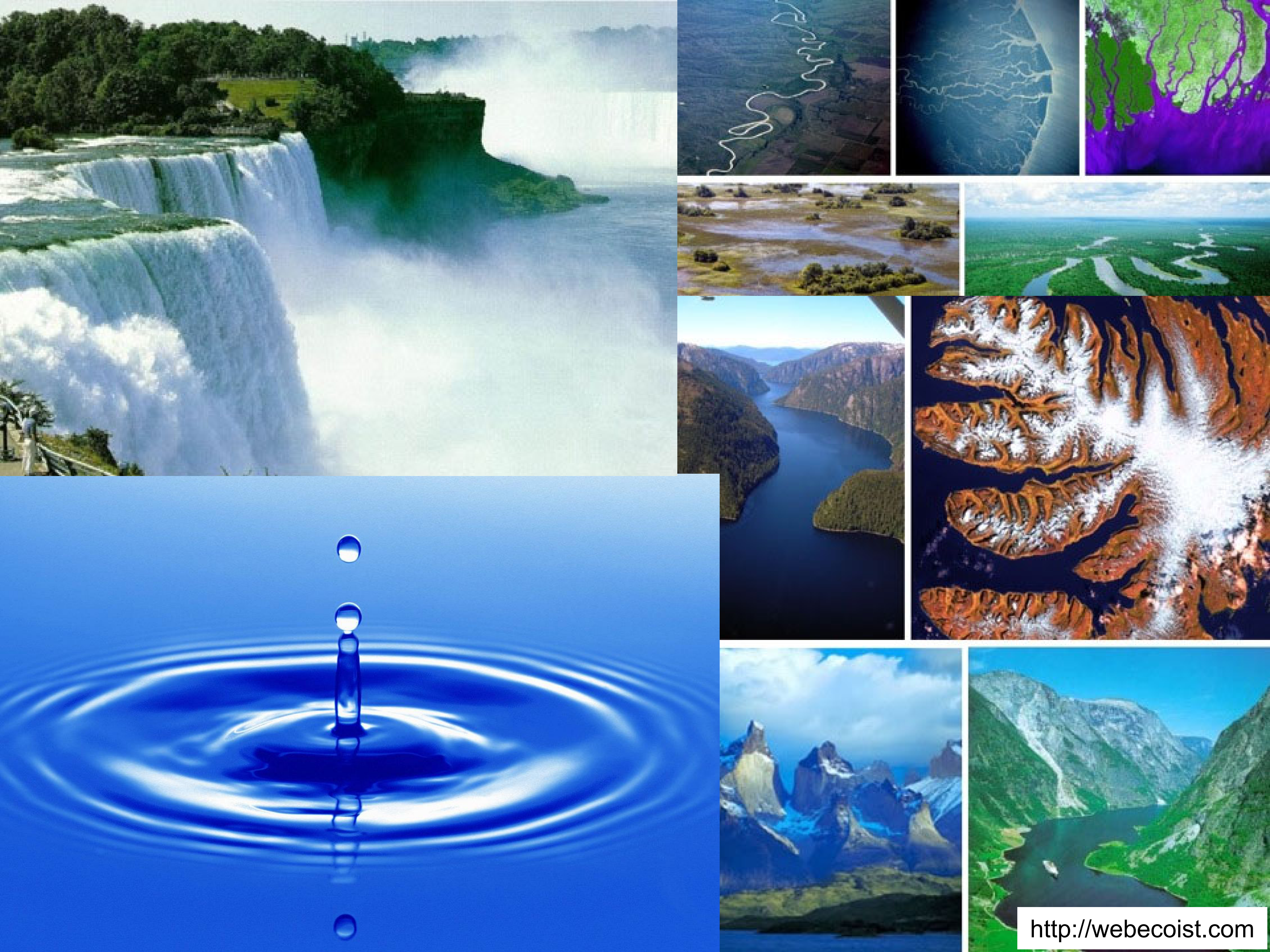


NP assembly chemistry

NP-supported metal oxides



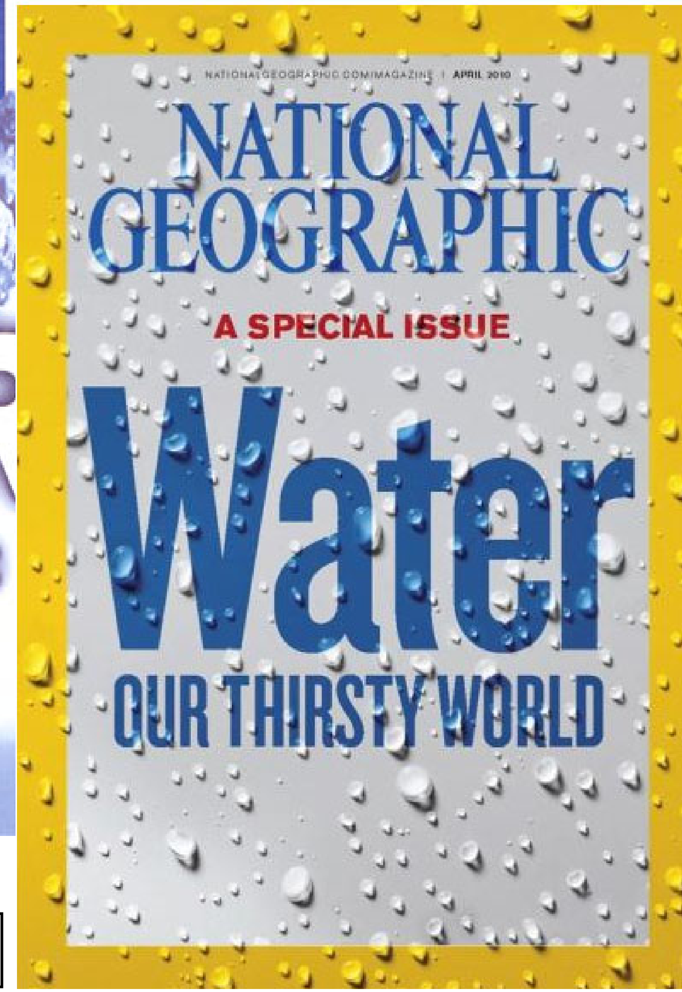
Catalysis fundamentals through materials


http://webecoist.com

20 March, 2008

Sep. 22, 1980

Aug. 12, 2002



April 2010

http://projects.nytimes.com/toxic-waters

Toxic Waters

A series about the worsening pollution in American waters and regulators' response

http://www.un.org/waterforlifedecade/

2007 CERCLA list

- **DNAPL**: **21** out of top 30
- Chlorinated hydrocarbons: 16 out of top 30

Rank	Substance Name
1	Arsenic
2	Lead
3	Mercury
4	Vinyl Chloride
5	**Polychlorinated Biphenyls (PCB)**
6	Benzene
7	Cadmium
8	**Polycyclic Aromatic Hydrocarbons**
9	**Benzo(A) Pyrene**
10	**Benzo(B) Fluoranthene**
11	**Chloroform**
12	**DDT, P,P'-**
13	**Aroclor 1254**
14	**Aroclor 1260**
15	**Dibenzo(A,H) Anthracene**

Rank	Substance Name
16	**Trichloroethylene (TCE)**
17	**Dieldrin**
18	Chromium, Hexavalent
19	Phosphorus, White
20	**Chlordane**
21	**DDE, P,P'-**
22	**Hexachlorobutadiene**
23	**Coal Tar Creosote**
24	**Aldrin**
25	**DDD, P,P'-**
26	**Benzidine**
27	**Aroclor 1248**
28	Cyanide
29	**Aroclor 1242**
30	**Aroclor**

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) list
at website of Agency for Toxic Substances and Disease Registry (http://www.atsdr.cdc.gov/cercla/).

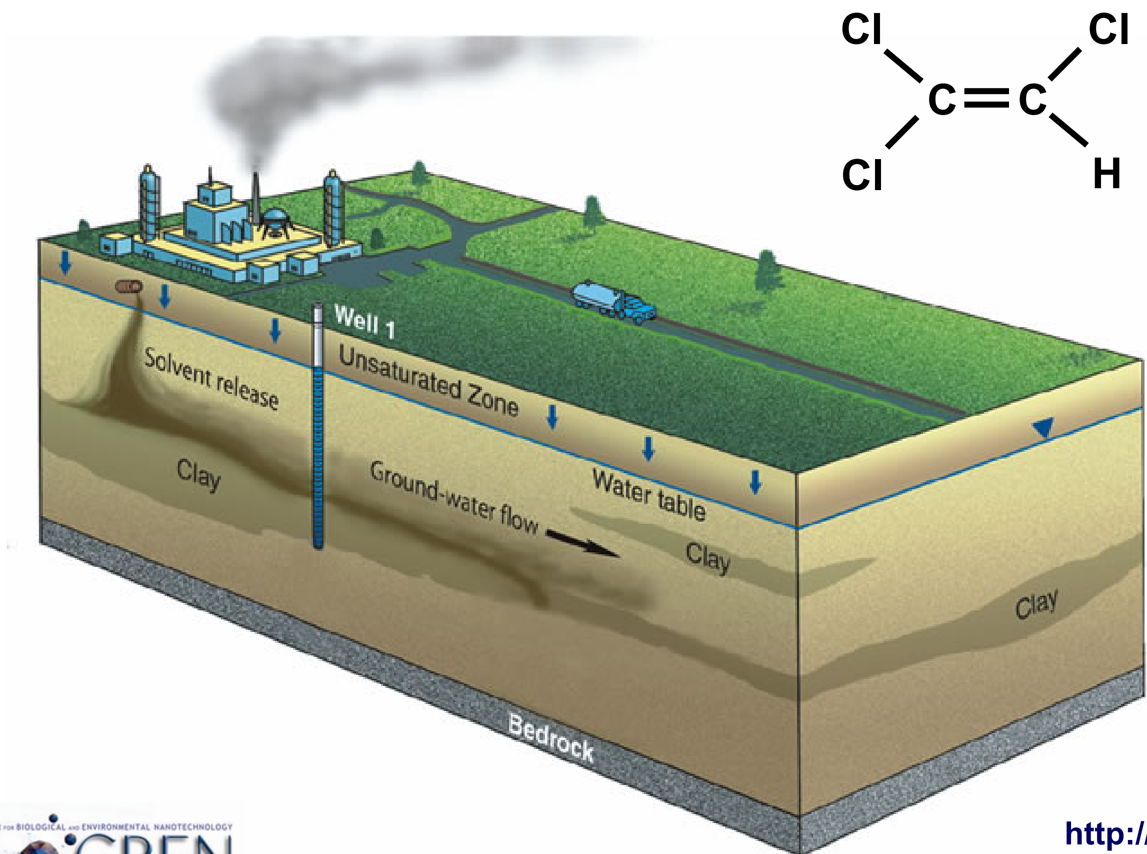
Trichloroethene (TCE) problem

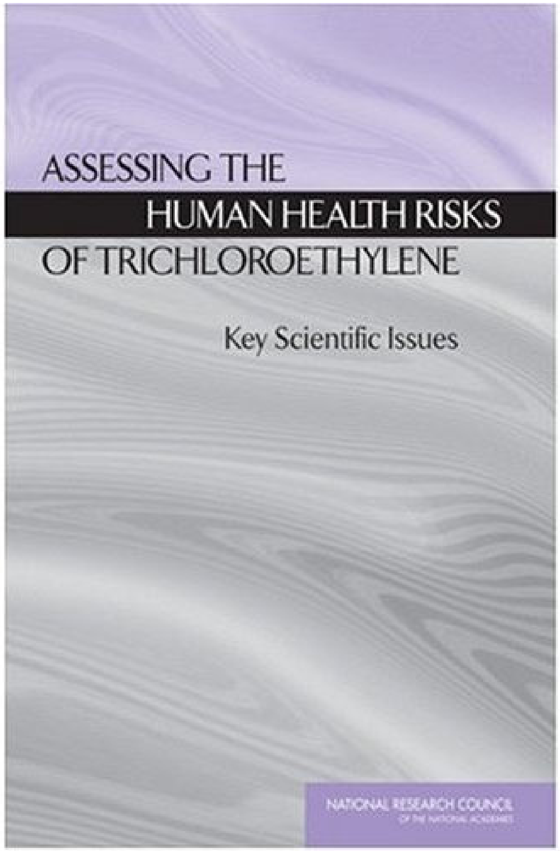
Widely used as a degreasing solvent

Found in 60% of Superfund sites

Highly persistent in groundwater, difficult to remove

Health effects: cancer, organ damage, developmental toxicity





(NRC, July 2006)

http://water.usgs.gov/nawqa/vocs/national_assessment/report/chapter5.html

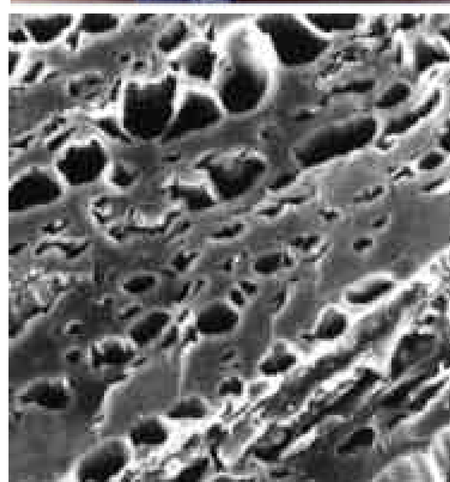
RICE

Water remediation strategy: adsorption

- Adsorption using activated carbon

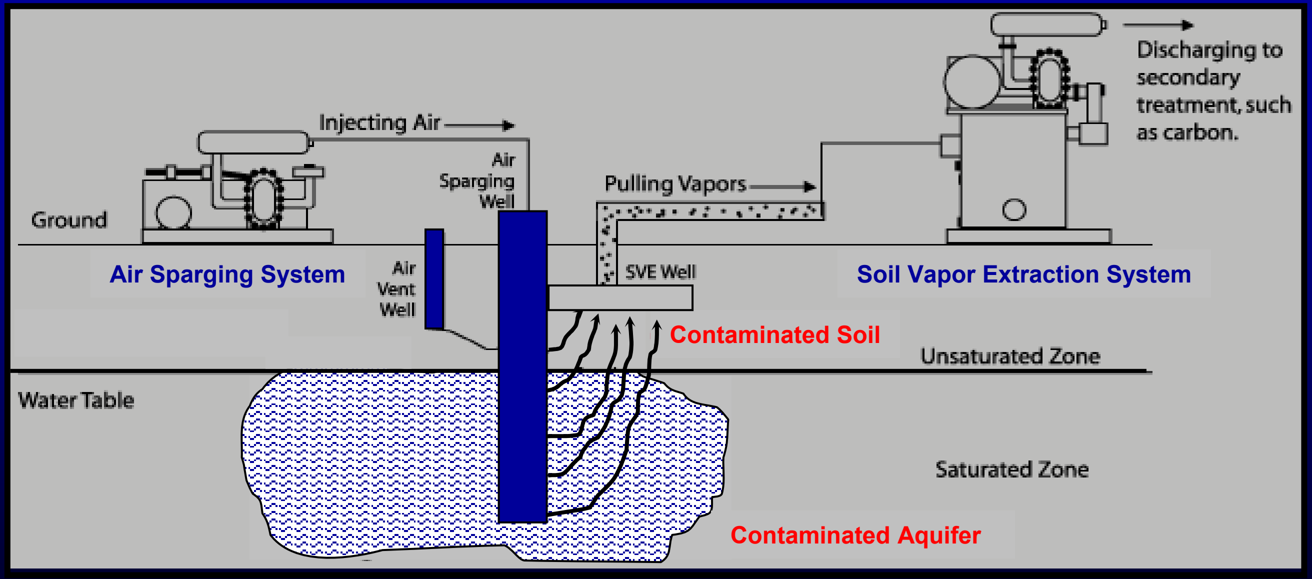
www.activated-carbon.com

www.tigg.com



Remediation technologies

- Carbon adsorption
  - Contaminated groundwater is pumped out of the aquifer and into a series of carbon beds (*i.e. ex situ* treatment)
  - TCE is transported from liquid to solid phase
- Air stripping
  - Contaminated groundwater is contacted with an air stream
  - In aquifer remediation possible (*in situ* treatment)
  - TCE is transported from liquid to gas phase



➡ Major drawback is the required further treatment (i.e. incineration)

Water remediation: chemical treatment

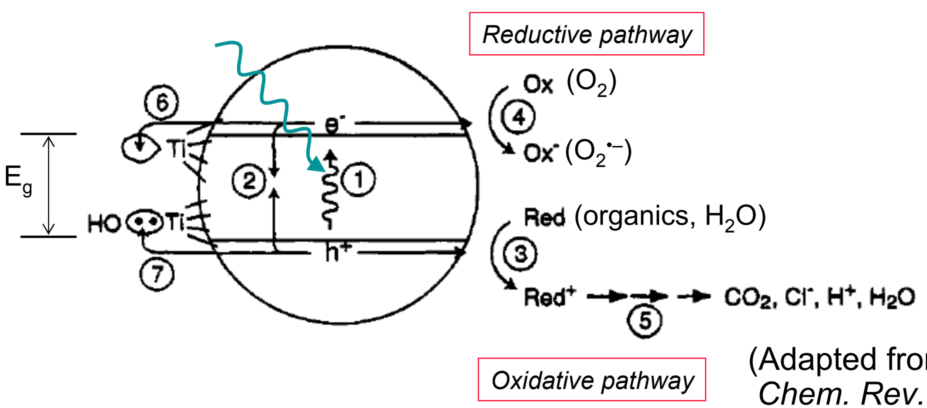
Examples include

- Bioremediation (use of microorganisms)
- Phytoremediation (use of plants)

- Titanium oxide (TiO_2) photocatalysis

+ UV light

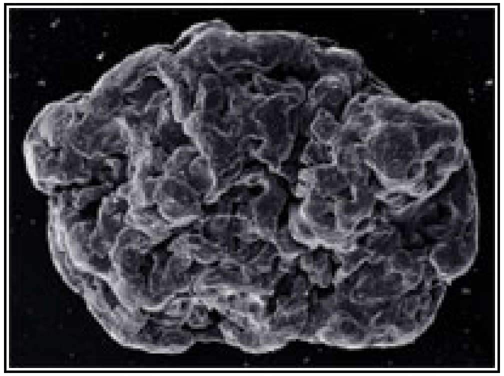
www.purifics.com



(Adapted from Hoffmann *et al.*, *Chem. Rev.*, 1995)

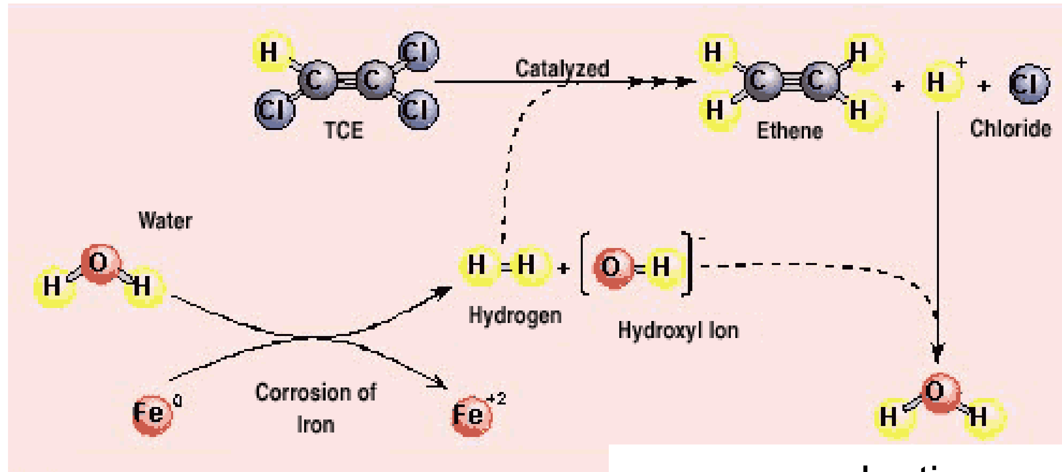
Chemical treatment: zero-valent iron

Pioneered by R. W. Gillham (early 1990's)



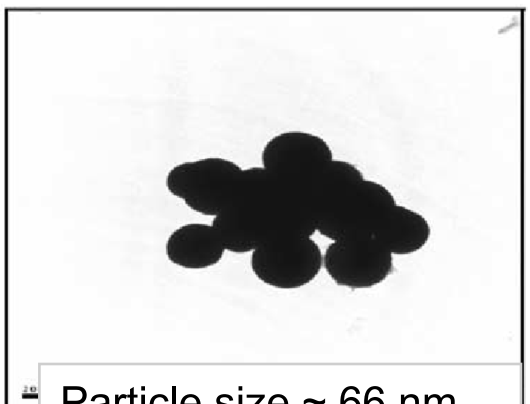
Particle size <74 microns
Surface area = 0.1 m^2/g

Hydrodechlorination (HDC) reaction:



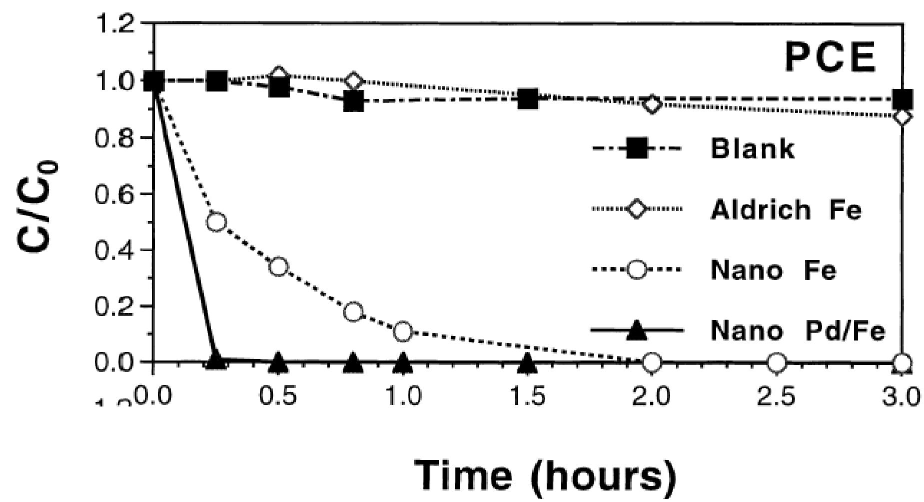
Ferox^{sm} Mechanism

www.zerovalentiron.com



Particle size ~ 66 nm
Surface area = 35 m^2/g

W.-X. Zhang, *J. Nanopart. Res.* **2003**, 5, 323-332

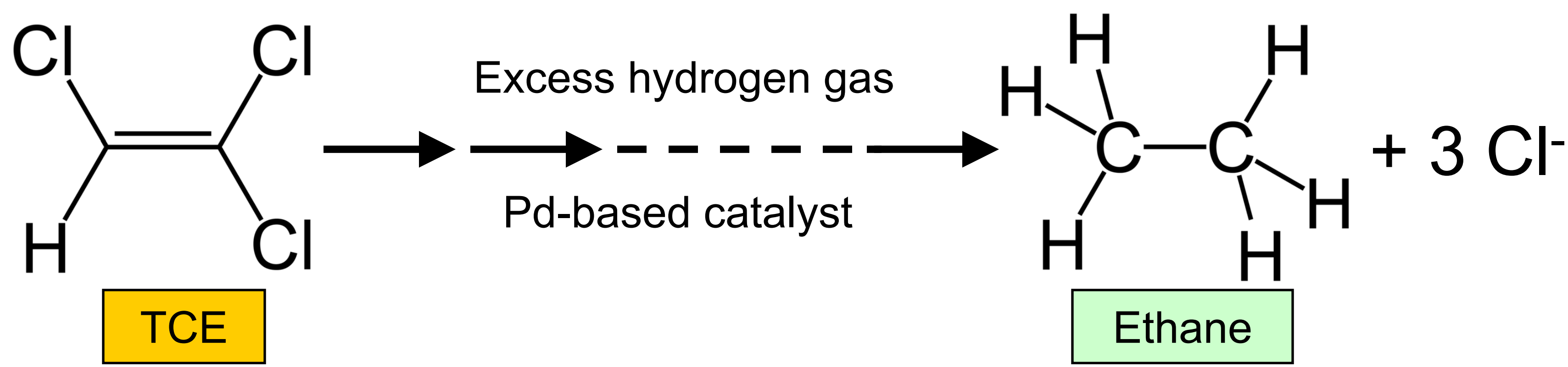


W.-X. Zhang et *al.*, *Catal. Today* **1998**, 40, 387-395

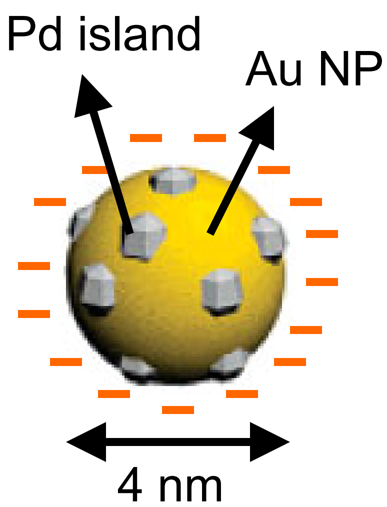
Trichloroethene hydrodechlorination

- Ranked 16th on Priority List; may lead to vinyl chloride (ranked 2nd)
  - Contaminates 60% of Superfund sites, EPA limit = 5 ppb
- Linked to organ damage and cancers

Treatment:
- Biodegradation can result in more hazardous vinyl chloride
- Conventional physical displacement methods (air-stripping and carbon adsorption) are not effective
  - move TCE from one phase to another—still requires further treatment
- Catalytic TCE hydrodechlorination (TCE HDC) is more desirable



Pd-on-Au nanoparticles (Pd/Au NPs)



- 4-nm Au NP synthesis
  1) $HAuCl_{4(aq)}$ 1 wt% 1 mL + water 80 mL (stir at 60°C heat)
  2) Tannic acid 0.05 g + Na_3Cit 0.04 g + K_2CO_3 0.018 g + water 20 mL (stir at 60°C heat)
  3) Add (2) into (1), keep stirring and boiling for 20 min
- Pd islands on Au NP surface
  1) Add certain amount (controlling Pd coverage) of 2.47 mM $HPdCl_{4(aq)}$ to 2 mL Au NP suspension; then mix
  2) Bubble H_2 gas (reducing Pd on Au NP) for 2 min
- Pd/Au NPs show >150 times activity than conventional Pd/Al_2O_3 catalyst for TCE HDC

Nutt et al., *Appl. Catal. B: Environ.*, 2006, *69*, 116.

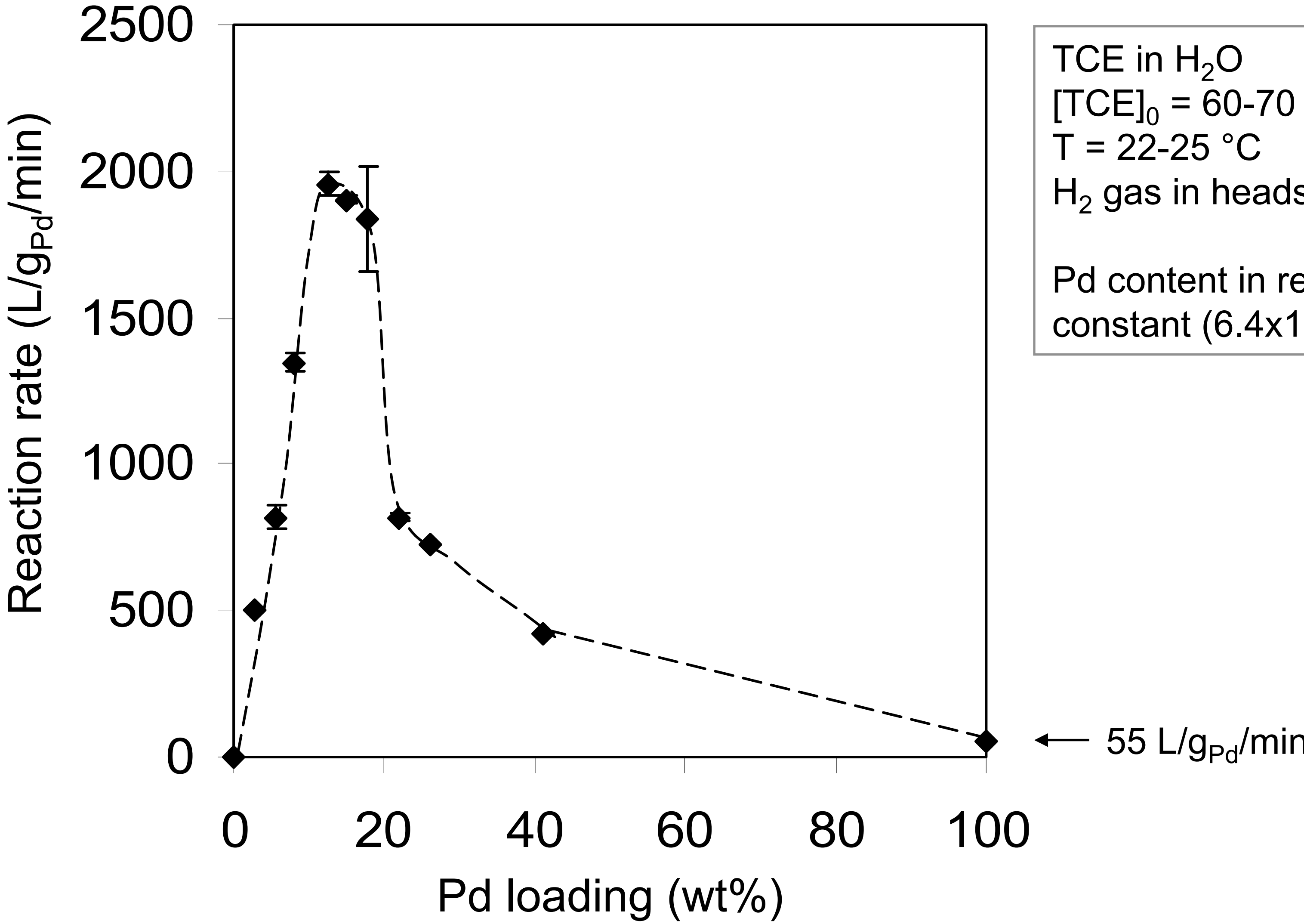
TCE HDC – commonly assumed as 1st order reaction

$$\boxed{\frac{-d[TCE]}{dt} = k[TCE]}$$

Catalyst type	Rate constant k ($L/g_{Pd}/min$)*
Pd black	1.4
Pd/Al_2O_3 powder	25.6
Pd NP (4 nm)	55.0
Pd/Au NP (4 nm, 60% Pd coverage)	1900

* Initial [TCE] = 60~70 ppm

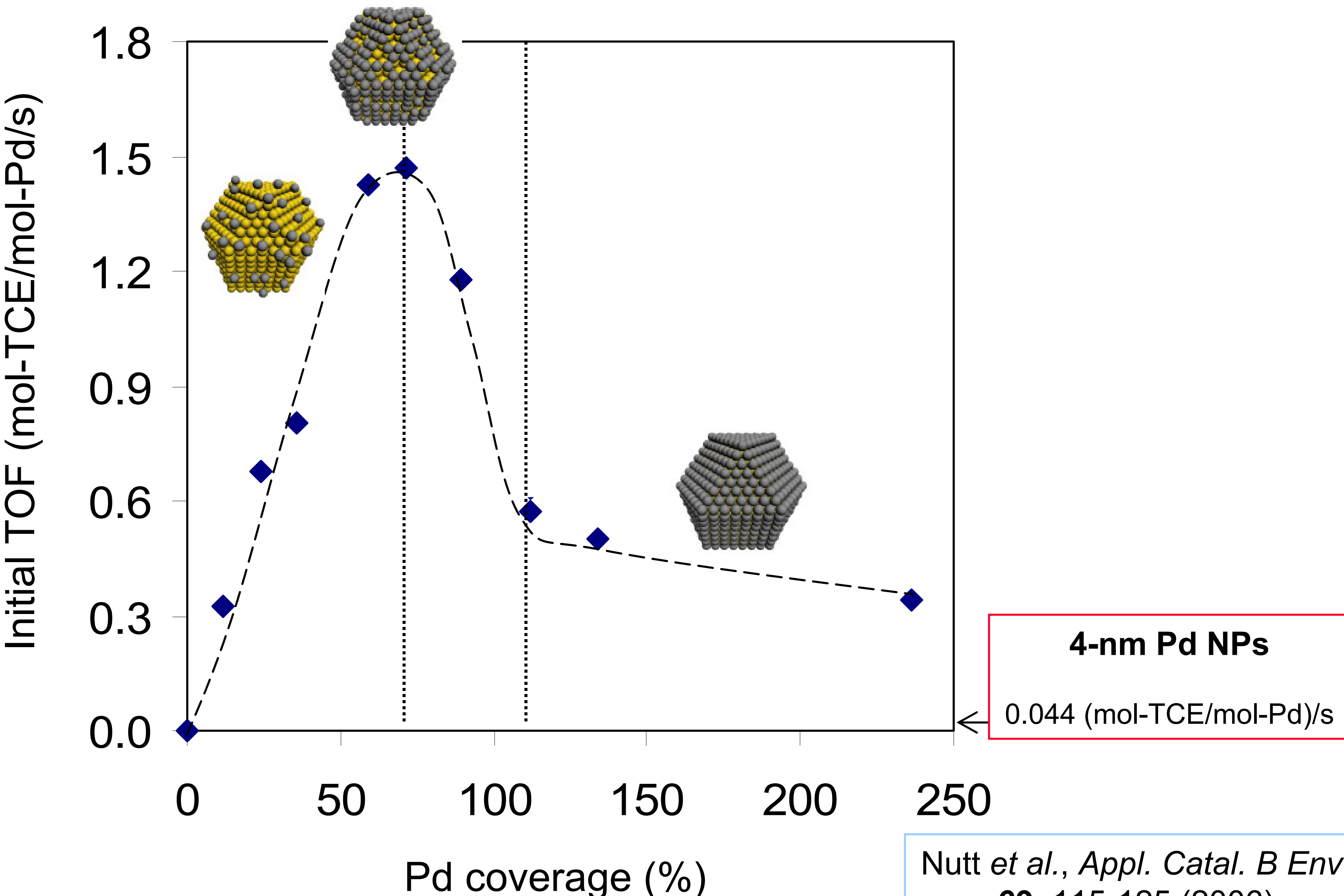
Reaction rate as function of wt% Pd



TCE in H_2O
$[TCE]_0$ = 60-70 ppm
T = 22-25 °C
H_2 gas in headspace

Pd content in reactor was constant ($6.4x10^{-8}$ moles)

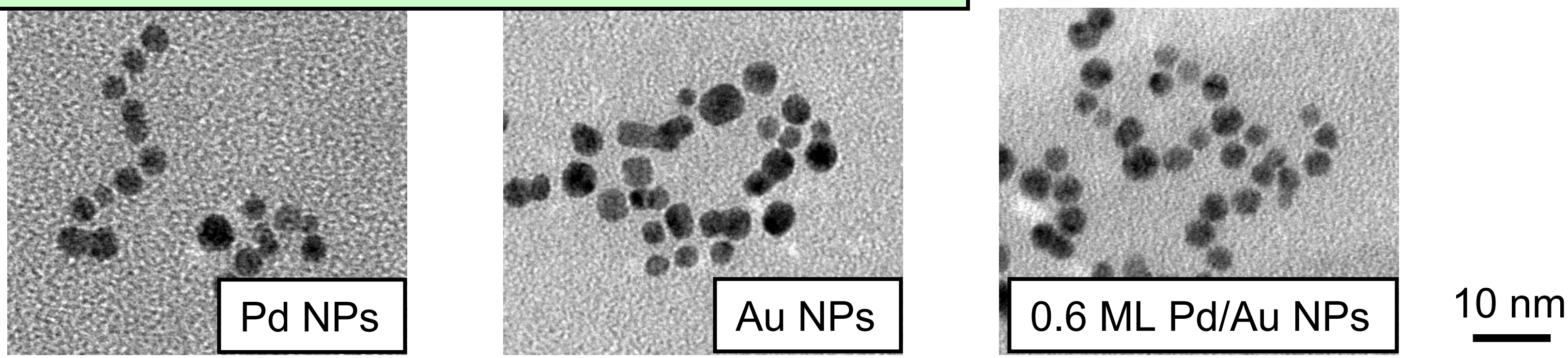
Nanostructure has strong influence



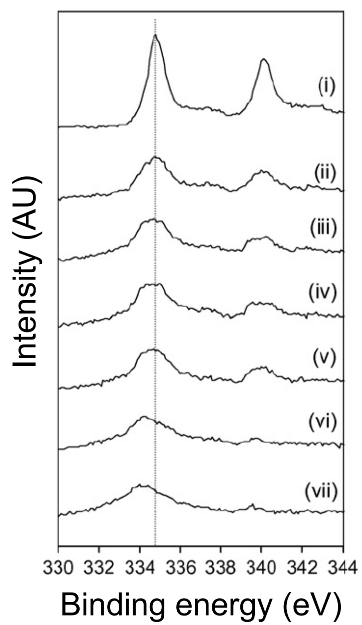
Nutt *et al.*, *Appl. Catal. B Env.* **69**, 115-125 (2006)

Indirect evidence for Pd/Au nanostructure

Pd-on-Au nanostructure not observed through TEM



XPS shows Pd in contact with Au on Pd/Au NPs



Pd NPs

300% ML Pd/Au NPs

200% ML Pd/Au NPs

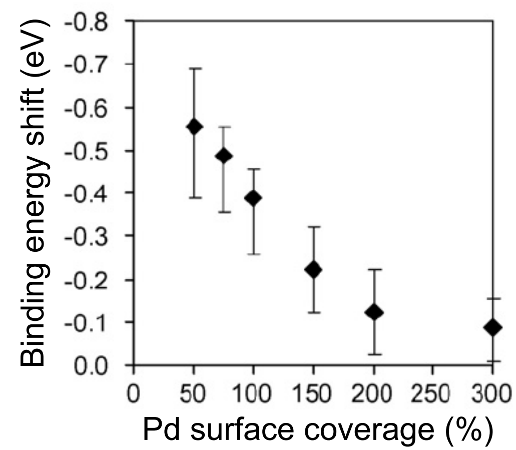
150% ML Pd/Au NPs

100% ML Pd/Au NPs

75% ML Pd/Au NPs

50% ML Pd/Au NPs

Pd binding energy shifts as a function of Pd surface coverage



Nutt et al., *Appl. Catal. B: Environ.*, 2006, *69*, 116.

EXAFS results – Pd/Au NPs

Calculated from atomic ratio

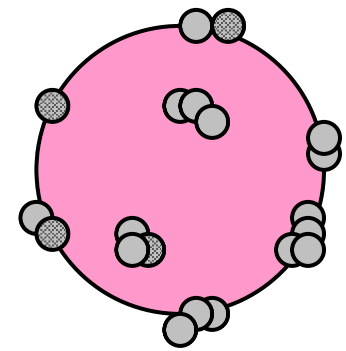
Edge	Treatment	Scattering path	N	N_{random}
Pd	Air RT	Pd-O	0.9	
		Pd-Pd	3.3	**1.3**
		Pd-Au	4.0	**6.0**

Pd ~20% oxidized
Pd islands
(more Pd-Pd neighbors)

Edge	Treatment	Scattering path	N	N_{random}
Au	Air RT	Au-Au	9.6	**8.9**
		Au-Pd	1.3	**2.0**

Au 100% metallic
Au-rich core
(therefore, Pd-rich shell)

Pd/Au NPs



4% H_2/He 300°C 30min

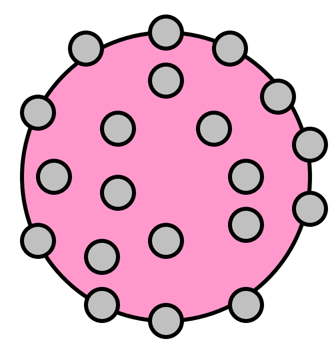
He 200°C

Edge	Treatment	Scattering path	N	N_{random}
Pd	H_2 300 °C, He 200 °C, He RT	Pd-Pd	2.0	**2.0**
		Pd-Au	6.9	**6.9**

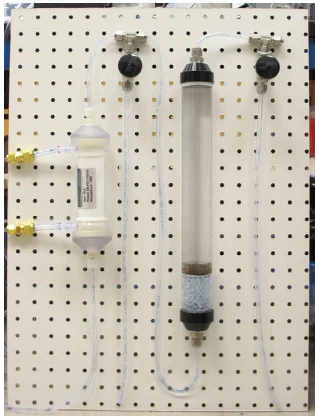
Pd 100% metallic
Pd random distribution

Edge	Treatment	Scattering path	N	N_{random}
Au	H_2 300 °C, He 200 °C, He RT	Au-Au	9.3	**8.5**
		Au-Pd	1.6	**2.4**

Au 100% metallic
Au-rich core
(therefore, Pd-rich shell)

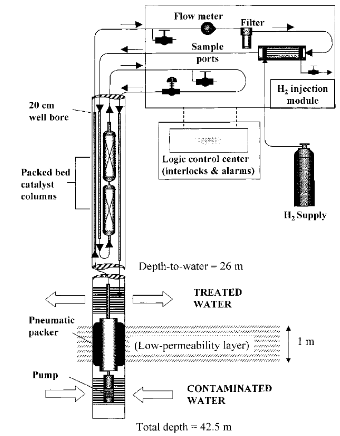


Comparison of materials cost



Pd/Au-NP/IER

Pd/Al_2O_3



McNab et al., *Environ. Sci. Technol.*, **2000**, *34*, 149.

<u>$k = 8.4 \times 10^7$ L/kg_{Pd}/day</u>

<u>$k = 5.3 \times 10^4$ L/kg_{Pd}/day</u>

For example, to treat 1000 L (~1 ton) water (100 ppm to 5 ppb TCE) in 2 days (flowrate = 0.35 L/min),

Total Pd needed: 0.0589 g
Total Au needed: 0.343 g
Total IER needed: 9404 g

IER: $0.014 USD/g
Spot prices (Oct. 12, 2007):
Pd: $377 USD/oz
Au: $748 USD/oz

<u>Overall price: $135</u>

Total Pd needed: 94.17 g
That is, total Pd(1 wt%)/Al_2O_3 needed: 9417 g

Pd/Al_2O_3: $0.27 USD/g

<u>Overall price: $2543</u>

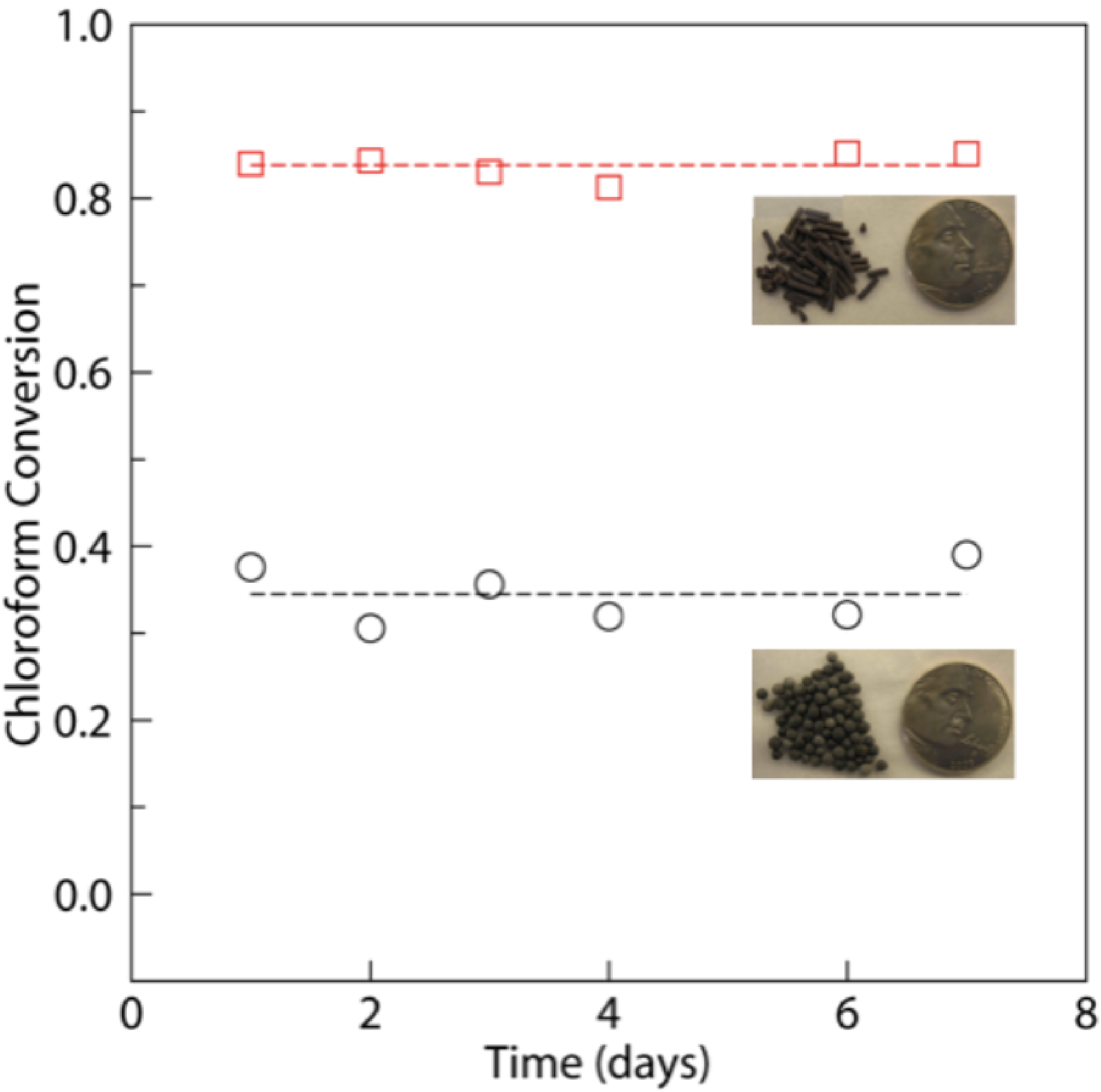
Other chlorinated C_2's can be removed

Table 2. HDC rate constants for selected chlorinated ethenes, using 4 nm Pd-on-Au NPs (with 25% Pd coverage). Reaction conditions are the same as above.[44]

Compound		Rate constant ($L\ g^{-1}_{Pd}\ min^{-1}$)	C–Cl bond strength ($kJ\ mol^{-1}$)[31,45]
PCE	$Cl_2C{=}CCl_2$	270	381
TCE	$ClHC{=}CCl_2$	858	391
1,1-DCE	$H_2C{=}CCl_2$	1519	393
cis-DCE	$ClHC{=}CHCl$	1813	370
trans-DCE	$ClHC{=}CClH$	2303	371

From M.S. Wong, P. J.J. Alvarez, Y.L. Fang, N. Akcin, M. O. Nutt, J. T. Miller, K. N. Heck, "Cleaner Water using Bimetallic Nanoparticle Catalysts" J. Chem. Tech. & Biotech. 84, 158-166 (2009).

Flow reactor results for chloroform HDC



$Pd/Au/Al_2O_3$

Average Flow Rate	~1	mL/min
CF Concentration	15	mg/L
Experiment duration	7	Days

2 wt% Pd/Al_2O_3

Average Flow Rate	~1	mL/min
CF Concentration	15	mg/L
Experiment duration	7	Days

Summary and conclusions

- Nanostructured materials can be engineered to treat contaminated water
  – Filtration, adsorption, chemical, catalytic approaches
- Pd-on-Au bimetallic NPs break down chlorinated compounds (via reductive catalysis)
  – Pd-on-Au catalysts work 100x better than Pd-only ones
- Desired form of nanocatalysts in applications: immobilized on a support, not in free suspension
- Catalysis is a promising approach to treat contaminated water
  – Greater efficiencies → smaller-footprint units?
  – Room-temperature reactions → no heating energy required
  – Can treat multiple contaminants simultaneously